

Europium doped thiosilicate phosphors of the alkaline earth metals Mg, Ca, Sr and Ba: structure and luminescence

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Eu-doped thiosilicate phosphors are promising materials to be used as wavelength converters in LEDs. They generally furnish a broad excitation spectrum which overlaps with the emission of many commercially available UV and blue LEDs. Moreover, their emission colour can be tuned from blue to red by changing the alkaline earth metal on the one side (Fig. 1), and by choosing Eu^{2+} or Ce^{3+} as an activator on the other side. Also, the quantum efficiency of the thiosilicates is acceptable (e.g. 30% for Sr_2SiS_4 , 35% for Ca_2SiS_4) and open to further improvement, e.g. by fine-tuning the synthesis conditions [1].

The thermal quenching temperature $T_{0.5}$ (defined as the temperature for which the emission intensity is half of the intensity at low temperature) in $\text{Ca}_2\text{SiS}_4\text{:Eu}$ is sufficiently high (470K), but lower for $\text{Sr}_2\text{SiS}_4\text{:Eu}$ (380K) [2,3]. From an application point of view, the stability against moisture of the alkaline earth thiosilicates is a matter of concern, but techniques to improve this have been proposed [4].

The luminescent characteristics of the Eu-ions in the thiosilicates are linked to the structural characteristics. This was demonstrated with the study of $(\text{Ca,Sr})_2\text{SiS}_4$ [3], where the two emission bands of these thiosilicates originate from the two inequivalent sites of the europium ions. Due to the different crystallographic structures of Ca_2SiS_4 and Sr_2SiS_4 , phase segregation occurs in $\text{Ca}_{2x}\text{Sr}_{2-2x}\text{SiS}_4$ when $0.5 < x < 0.9$. This was observed by x-ray diffraction analysis and cathodoluminescence studies at the microscopic level [3].

Here we also report on the $(\text{Ca,Mg})_2\text{SiS}_4$ -system. In the orthorhombic Ca_2SiS_4 -phase, a substitution of a small percentage of Ca^{2+} by Mg^{2+} shifts the emission spectrum to longer wavelengths. Similarly, in the Mg_2SiS_4 -phase a small percentage of Mg^{2+} can be substituted by Ca^{2+} , shifting the emission peaks. Intermediate multiphase compositions exhibit more complex PL spectra.

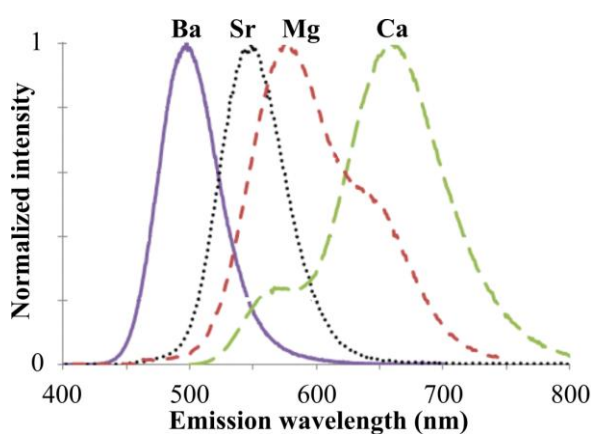


Fig. 1. Emission spectra of thiosilicates doped with 2% Eu.

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